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(54) MEASURING METHOD FOR TRACE MOISTURE

(57)Abstract:
PURPOSE: To measure the trace moisture in ammonia gas with high accuracy by thermally decomposing the ammonia gas into the decomposed mixed gas constituted of nitrogen, hydrogen, and water with a noble metal catalyst, and measuring the moisture in the decomposed mixed gas.
CONSTITUTION: The ammonia gas from an ammonia gas cylinder 1 is regulated to the prescribed pressure by a pressure reducing valve 2, it is regulated to the prescribed flow, i.e., space velocity in the range of 300-1000hr-1, by a flow indicator 3, and it is introduced into a catalyst tank 4 heated preferably to 600-1000°C and filled with a noble metal catalyst for thermal decomposition. The mixed gas formed into three constituents of nitrogen, hydrogen, and moisture by this thermal decomposition is cooled by a cooling device 5 then guided to a moisture measuring device 6, and the moisture is measured. The noble metal catalyst is not limited in particular, and palladium, ruthenium, or platinum is preferable because it substantially decomposes ammonia completely. The trace moisture of about 1-10ppm in the ammonia gas can be simply and accurately measured.

CLAIMS

[Claim 1] The measuring method of the minute amount moisture in the ammonia gas which pyrolyzes the ammonia gas containing minute amount moisture using a noble metal catalyst, considers as the decomposition mixed gas which consists of nitrogen, hydrogen, and moisture, and is characterized by measuring the moisture in the aforementioned decomposition mixed gas.
[Claim 2] The measuring method of the minute amount moisture in the ammonia gas according to claim 1 whose minute amount moisture is 0.1-10 ppm.
[Claim 3] The measuring method of the minute amount moisture in the ammonia gas according to claim 1 or 2 whose noble metal catalyst is palladium.
[Claim 4] The measuring method of the minute amount moisture in the ammonia gas according to claim 1 or 2 whose noble metal catalyst is a ruthenium.
[Claim 5] The measuring method of the minute amount moisture in the ammonia gas according to claim 1, 2, 3, or 4 whose temperature of a pyrolysis is 600-1000 °C.
[Claim 6] The measuring method of the minute amount moisture in the ammonia gas according to claim 1, 2, 3, 4, or 5 whose water measurement in decomposition mixed gas is what is carried out using an optical dew-point instrument.

[Claim 7] The measuring method of the minute amount moisture in the ammonia gas according to claim 1, 2, 3, 4, or 5 whose water measurement in decomposition mixed gas is what is carried out using an infrared-absorption-spectrum method.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to the measuring method of the minute amount moisture contained in the above-mentioned ammonia gas in more detail about the purity measuring method of the high grade ammonia gas used in a semiconductor manufacture field etc.
[0002]
[Description of the Prior Art] Conventionally, as a measuring method of the moisture contained in ammonia gas, the ammonia gas thermal decomposition method by the gas-chromatography method (the GC method), the infrared-absorption-spectrum method (the FT-IR method), the SEMI standard (SEMI Japan standard publication), etc. is known.
[0003] Since a minimum-limit-of-detection community is about 10 ppm, the GC method is not suitable for measurement of the moisture of a minute amount or a ultralow volume. By the FT-IR method, since the absorption noise of NH entered, an error tended to go into the analysis of moisture based on the stretching vibration of OH, and when the moisture contained in ammonia gas was a minute amount, there was a fault which lacks in the reliability of analysis precision a certain degree.
[0004] The method by the SEMI standard (SEMI C3, 12-94) is the method of measuring the moisture which was not decomposed by measuring a dew-point, after heating the ammonia gas containing moisture at about 950 °C, pyrolyzing through and ammonia to the catalyst tub filled up with the nickel system catalyst and decomposing into nitrogen and hydrogen.
[0005] However, by the method by the SEMI standard, since the moisture which the nickel oxide contained in a nickel system catalyst was returned by hydrogen, consequently was generated was also measured simultaneously, there was a problem which will show a moisture content always higher than the moisture originally contained in ammonia gas. therefore, the method of measuring simply and correctly the moisture of the about 0.1-10 ppm minute amount in the high grade ammonia gas which is especially a semiconductor manufacture field and is needed now is not learned
[0006]
[Problem(s) to be Solved by the Invention] this invention aims at offering the method of measuring the moisture in the ammonia gas containing the moisture of an about 0.1-10 ppm minute amount in a high precision in view of the above.
[0007]
[Means for Solving the Problem] The summary of this invention pyrolyzes the ammonia gas containing minute amount moisture using a noble metal catalyst, considers as the decomposition mixed gas which consists of nitrogen, hydrogen, and moisture, and is in the place which measures the moisture in the aforementioned decomposition mixed gas. Since a noble metal catalyst originally does not contain an oxide substantially, it can measure only the minute amount moisture which does not generate moisture by the

hydrogen reduction like [at the time of using the above-mentioned nickel system catalyst], and is contained in ammonium gas.
[0008] Drawing 1 is used for below and the embodiment of this invention is concretely explained to it. The ammonia gas which came out of the ammonia chemical cylinder 1 is 2kg [0.1-3 //cm] by the reducing valve 2. It is adjusted to a predetermined pressure, a predetermined flow rate (simian virus), i.e., space velocity, is adjusted by the flow indicator 3 by the range of 300-1000hr-1, and it goes into the catalyst tub 4. The catalyst tub 4 is filled up with 600-1000 °C of noble metal catalysts preferably heated by 700-1000 °C, and ammonia gas is pyrolyzed while passing the catalyst tub 4. It is cooled with a cooling system 5, the mixed gas used as three components of nitrogen, hydrogen, and moisture is led to water measurement equipment 6, and moisture is measured by the above-mentioned pyrolysis.
[0009] Since it is not limited especially as a noble metal catalyst used in this invention, for example, palladium, a ruthenium, platinum, an osmium, iridium, a rhodium, etc. can be mentioned and ammonia is decomposed altogether substantially especially, palladium, a ruthenium, and platinum are desirable.
[0010] When using palladium as the above-mentioned noble metal catalyst, the palladium catalyst of marketing, such as a thing which made the alumina, the silica, etc. support 0.5 % of the weight of palladium, can be used. When using a ruthenium as the above-mentioned noble metal catalyst, the ruthenium catalyst of marketing, such as a thing which made the alumina, the silica, etc. support 0.5 % of the weight of rutheniums, can be used.
[0011] Especially the above-mentioned water measurement equipment 6 is not limited, for example, can use well-known things, such as a crystal oscillation formula moisture meter, an electrostatic-capacity formula moisture meter, an optical dew-point instrument, and an infrared spectrophotometer, and an optical dew-point instrument and its infrared spectrophotometer are desirable from standpoints, such as simplicity of measurement, and accuracy, especially.
[0012] Since this invention is replaced with a nickel system catalyst and noble metal catalysts, such as palladium, a ruthenium, platinum, an osmium, iridium, and a rhodium, are used for it when pyrolyzing ammonia gas, it can measure only the moisture which does not generate any moisture other than the ammonia gas origin by the hydrogen reduction like [at the time of using a nickel system catalyst], and is contained in ammonia gas.
[0013]
[Example] Although an example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these examples.
[0014] an example 1 -- pressurization rectification and moisture removal according the ammonia gas measured with 50 ppm in the moisture content by the gas-chromatography method to an adsorbent were beforehand diluted 5 times using the anhydrous-ammonia gas which repeated several times by turns and was obtained and which does not contain moisture substantially, and the ammonia gas containing the moisture of 10 ppm was prepared Uniform restoration of the 20g of the catalysts which made palladium support this gas with the flow rate of 0.1 Nl/min (simian-virus=300hr-1) 0.5% of the weight was carried out, and it introduced into the catalyst tub heated at 900 °C. After performing the pyrolysis of ammonia, when cracked gas was led to the optical mirror formula dew-point

instrument and the dew-point of cracked gas was measured, moisture was measured with 4.8 ppm at -65.7 °C. When ammonolysis gas was converted into the moisture in ammonia gas, it was set to 9.6 ppm from the quantitas duplex of the volume before the volume decomposing, and the bird clapper, and it was measured in a high precision.

[0015] Ammonia gas with a moisture of 10 ppm used in the example 2 example 1 was diluted with anhydrous-ammonia gas, and the ammonia gas containing the moisture of 4 ppm was prepared. Uniform restoration of the 25g of the catalysts which made the ruthenium support this gas with the flow rate of 0.3 Nl/min (simian-virus=900hr-1) 0.5% of the weight was carried out, and it introduced into the catalyst tub heated at 850 °C. After performing the pyrolysis of ammonia, when cracked gas was led to the optical mirror formula dew-point instrument and the dew-point of cracked gas was measured, moisture was measured with 2.0 ppm at -71.7 °C. When ammonolysis gas was converted into the moisture in ammonia gas from the quantitas duplex of the volume before the volume decomposing, and the bird clapper, it was 4.0 ppm.

[0016] Ammonia gas with a moisture of 10 ppm used in the example 3 example 1 was diluted with anhydrous-ammonia gas, and the ammonia gas containing the moisture of 1 ppm was prepared. Uniform restoration of the 28g of the catalysts which made the ruthenium support this gas with the flow rate of 0.3 Nl/min (simian-virus=900hr-1) 0.5% of the weight was carried out, and it introduced into the catalyst tub heated at 950 °C. After performing the pyrolysis of ammonia, when cracked gas was led to the optical mirror formula dew-point instrument and the dew-point of cracked gas was measured, it was -79.2 °C. Like the example 1, when converted into the moisture in ammonia gas, it was 1.2 ppm.

[0017] an example 4 -- the anhydrous nitrogen gas which does not contain moisture substantially beforehand was introduced into the diffusion pipe type moisture generator, the nitrogen gas of 10 ppm of moisture contents was obtained, this was led to the 10m long optical-path gas cell of Fourier-transform-infrared-spectroscopy equipment (FT-IR), and the absorbance of the 3740cm-1 neighborhood based on the stretching vibration of OH was measured The absorbance was measured with 0.0160 and, thereby, created the one-point calibration curve. On the other hand, ammonium gas with a moisture of 10 ppm used in the example 1 was diluted with anhydrous ammonium gas, and the ammonium gas containing the moisture of 4 ppm was prepared. 25g uniform restoration of this gas of catalysts which made the ruthenium support with the flow rate for 0.3Nl/(simian-virus=900h-1) 0.5% of the weight was carried out, and it was introduced into the catalyst tub heated at 850 °C. After performing the pyrolysis of ammonia, when it led cracked gas to the 10m long optical-path gas cell of Fourier-transform-infrared-spectroscopy equipment and the absorbance of the 3740cm-1 neighborhood based on the stretching vibration of OH was measured, it was measured with 0.0032. The fixed quantity of the part for gas Nakamizu at that time was carried out to 2.0 ppm from the calibration curve. Since ammonium cracked gas became the quantitas duplex of the volume before the volume decomposing, when converted into the moisture in ammonium gas, it was set to 4.0 ppm, and the moisture of sample offering gas and good coincidence were obtained.

[0018] Uniform restoration of the 25g of the catalysts, which made nickel support with the flow rate of 0.1 Nl/min (simian-virus=300hr-1) ammonia gas with a moisture of 10 ppm used in the example of comparison 1 example 1 10% of the weight was carried out, and it introduced into the catalyst tub heated at 950 °C. After performing the pyrolysis of

ammonia, when cracked gas was led to the optical mirror formula dew-point instrument and the dew-point of cracked gas was measured, it was -20 °C or more. Like the example 1, when converted into the moisture in ammonia gas, it was 2000 ppm or more.
[0019]
[Effect of the Invention] Since this invention pyrolyzes the ammonia gas containing the minute amount moisture of about 0.1-10 ppm using a noble metal catalyst and measures the moisture in decomposition mixed gas, it can measure minute amount moisture in a high precision.

TECHNICAL FIELD

[Industrial Application] this invention relates to the measuring method of the minute amount moisture contained in the above-mentioned ammonia gas in more detail about the purity measuring method of the high grade ammonia gas used in a semiconductor manufacture field etc.

PRIOR ART

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EFFECT OF THE INVENTION

[Effect of the Invention] Since this invention pyrolyzes the ammonia gas containing the minute amount moisture of about 0.1-10 ppm using a noble metal catalyst and measures

the moisture in decomposition mixed gas, it can measure minute amount moisture in a high precision.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention aims at offering the method of measuring the moisture in the ammonia gas containing the moisture of an about 0.1-10 ppm minute amount in a high precision in view of the above.

MEANS

[Means for Solving the Problem] The summary of this invention pyrolyzes the ammonia gas containing minute amount moisture using a noble metal catalyst, considers as the decomposition mixed gas which consists of nitrogen, hydrogen, and moisture, and is in the place which measures the moisture in the aforementioned decomposition mixed gas. Since a noble metal catalyst originally does not contain an oxide substantially, it can measure only the minute amount moisture which does not generate moisture by the hydrogen reduction like [at the time of using the above-mentioned nickel system catalyst], and is contained in ammonium gas.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The schematic diagram of the measuring method of the minute amount moisture of this invention.

[Description of Notations]

1 Ammonia Chemical Cylinder
2 Reducing Valve
3 Flow Indicator
4 Catalyst Tub
5 Cooling System
6 Water Measurement Equipment